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**(19) (CA) APPLICATION FOR CANADIAN PATENT (12)**

(54) Coating Media and Their Use for the Production of  
Acid-Resisting Coatings

(72) Flosbach, Carmen - Germany (Federal Republic of) ;  
Frigge, Eva - Germany (Federal Republic of) ;  
Schubert, Walter - Germany (Federal Republic of) ;

(71) Herberts Gesellschaft mit beschränkter Haftung - Germany  
(Federal Republic of) ;

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**Notice:** This application is as filed and may therefore contain an  
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Herberts Gesellschaft mit beschränkter Haftung

5     Coating media and their use for the production of acid-resisting coatings

10    This invention relates to a coating medium which is suitable for the production of acid-resisting coatings, particularly clear- and covering lacquer coatings, and which is suitable, for example, for the production of multilayer coatings in the motor vehicle industry.

15    Increasingly heavy demands are being made on the coatings used for vehicles. In addition to high gloss and mechanical resistance, to stone impact for example, resistance to petrol and oil is required. Additional demands occur in the context of the changing environment, such as the so-called "acid rain". The coatings industry is therefore subjected to the 20 requirement of producing coating media for acid-resisting coatings and coatings which withstand other aggressive conditions, such as the long-term effects of animal excrement. The increased demand for acid-resistance also leads to more stringent test methods. Whereas lacquers were previously 25 tested using dilute acetic acid, the effect of up to 40 % sulphuric acid, in part at an increased temperature of up to 70°C, is now being investigated. As far as possible, the protective effect and the appearance of the lacquer should not change in the areas tested under these conditions. At 30 most, only a slight roughness of the surface may occur due to extreme acidic exposure of this type.

35    Another point of view which the coatings industry has to take into consideration is exposure to physiologically hazardous substances, e.g. carcinogens and mutagens. Compounds which are not completely harmless include isocyanates and aromatic solvents, for example. On exposure to lacquer vehicles based

on lacquer systems which crosslink via free isocyanate groups, volatile reactive isocyanates can constitute a hazard to operating personnel. Skin contact with isocyanate-containing coating media should also be avoided.

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For these reasons there are developments aimed at avoiding the use of reactive isocyanates in coating media, particularly in the motor vehicle industry. EP-A-0 034 720 describes oxazolidine-containing acrylate resins which crosslink with water or atmospheric moisture to form films. However, this system has the disadvantage that the hardening surface opposes the deeper penetration of water into the lower lacquer layers and prevents complete hardening there. Vehicle systems are disclosed in EP-A-0 050 249, for example, which comprise silicon-containing polymers. These polymers can react with moisture and crosslink via groups on the silicon atom which are susceptible to hydrolysis. These systems have the disadvantage that the crosslinking is dependent on the relative atmospheric humidity. On the other hand, it has to be ensured that no moisture can reach the coating medium during storage, since otherwise it can no longer be processed.

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US-A-4 408 018 describes acrylic polymers into which acetoacetate groups have been introduced. The latter should crosslink with  $\alpha, \beta$ -unsaturated esters. Strong bases are required as catalysts for this crosslinking reaction. These remain in the coating film after hardening and have an adverse effect on the properties of the coating, e.g. yellowing or clouding of clear lacquer films may occur.

DE-A-35 41 140, EP-A-0 160 824 and EP-A-0 310 011 describe hardener components and vehicle systems for the coatings industry. These comprise solvent-containing two-component systems (2K systems) which are produced based on a polyunsaturated acrylate resin and a hardener component with active CH, NH or SH groups. In order to achieve rapid, adequate crosslinking, compounds with a catalytic effect are

5 required in the lacquer system. Examples of catalysts which are used include: tertiary amines, amidines, guanidines, phosphanes and halides of quaternary ammonium compounds. The amount of catalysts may be up to 5 weight %. They are necessary in order to accelerate the hardening reaction; this can be assisted by an elevated temperature.

10 The known coating media have to be used as two-component systems. They contain catalytically active compounds and cannot therefore be formulated as single-component systems (1K systems). The maximum pot lives of catalyst-containing two-component systems, which are mixed immediately before application, are 48 hours; this means that thereafter the coating media can no longer be used. When these known coating  
15 media are used as clear or covering lacquers, they exhibit a reduced stability towards yellowing on exposure to light. In addition, the known coating media do not comply with the above-mentioned more stringent criteria for acid-resistance.

20 The prior unpublished German Patent Application P 41 33 704.2 describes a catalyst-free single-component coating medium in which a crosslinking agent with at least two acidic CH hydrogen atoms crosslinks with an acryloyl-functional compound.

25 The object of the present invention is the production of a coating medium which is free from reactive isocyanate, and which results in coatings which satisfy the more stringent requirements relating to acid-resistance and which do not exhibit yellowing.

30 It has been shown that this object can be achieved by means of a catalyst-free system which can be formulated as a single-component system and which contains:

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A) 10 - 90 weight % of one or more compounds acting as crosslinking agents with an average of at least two groups capable of alcoholysis,

5 B) 10 - 90 weight % of one or more (meth)acrylate copolymers, polyester- and/or polyurethane resins with at least one  $\alpha,\beta$ -unsaturated group bonded via the carbonyl carbon atom of carbonyl, ester and/or amide groups, with a C=C equivalent weight of 85 - 1800, and a number average molecular weight ( $M_n$ ) of 170 - 10,000 g/mole, and with an OH number of up to 350 mg KOH/g, wherein the weight percentages of components A and B are each based on the solid and add up to 100 weight %, and

10 C) 0.1 - 10 weight % of one or more thermally and/or photochemically activatable initiators,

15 D1) 0 - 20 weight % of one or more melamine resin crosslinking agents,

20 D2) 0 - 40 weight % of one or more blocked polyisocyanates,

25 E) 0 - 40 weight % of one or more (meth)acrylol-functionalised reactive thinners which are free from OH groups,

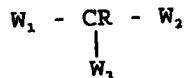
30 F) 0 - 30 weight % of one or more diols, triols, polyols and/or hydroxyfunctional polyethers, polyesters and/or (meth)acrylic copolymers and optionally solvents, the usual lacquer additives, optionally water, optionally pigments and optionally extenders.

35 It has been shown that a single-component coating medium such as this is capable of storage. It is applied without a

5 catalyst and after application can be crosslinked or hardened by heating to temperatures of 100-180°C. When photochemically activatable radical initiators are contained, hardening may be effected, by irradiation with UV light for example, at the same time as stoving or after stoving. The coatings obtained withstand a more stringent acid test, namely treatment with up to 40 % sulphuric acid at an elevated temperature up to 70°C. The coatings obtained exhibit good hardness.

10 The crosslinking agents used as component A) in the coating media according to the invention are preferably those which contain at least two groups which are capable of alcoholysis and which originate from one or more of the following groupings, which may be the same or different:

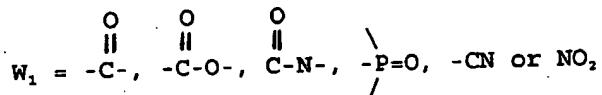
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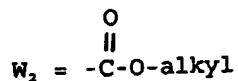
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where  $R$  = alkyl and preferably H,

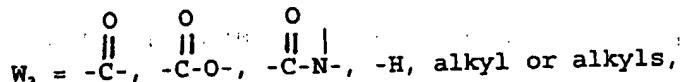
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wherein the alkyl and alkyls preferably comprise 1 to 6 C atoms, and wherein the carboxyl or carbonamide groups defined above for the  $W_1$ ,  $W_2$  and  $W_3$  radicals are each bonded to the CR group via the carbon atom and the CR group is bonded to a polymeric or oligomeric unit via at least one of the  $W_1$ ,  $W_2$

and/or  $W_1$  radicals. The functionality of component A) is on average  $> 2$  per molecule.

5 As stated above, the functionality of component A) is on average  $> 2$ . This means that monofunctional molecules may also be used in admixture with molecules of higher functionality.

10 The crosslinking components A) described above contain at least one ester group with  $W_1$ , which can crosslink with compounds containing hydroxyl groups in the sense of an alcoholysis reaction.

15 The crosslinking compounds are preferably substantially free from primary, secondary or tertiary amino groups, since these can have a negative effect on storage stability and lightfastness.

20 Examples of crosslinking components A) which are capable of alcoholysis and which correspond to the above general formula are given below. These examples are subdivided below into three groups: A1, A2, and A3.

25 In Group A1 the molecule contains an average of at least two groups which are derived from methanetricarboxylic acid monoamide units or acetoacetic acid ester-2-carboxylic acid amides.

30 Examples of suitable A1 compounds comprise reaction products of malonic acid diesters, such as malonic acid dimethyl, diethyl, dibutyl or dipentyl esters, or acetoacetic acid esters, such as acetoacetic acid methyl, ethyl, butyl or pentyl esters, with polyisocyanates.

35 Examples of isocyanates of this type which may be used according to the invention comprise cycloaliphatic, aliphatic or aromatic polyisocyanates such as tetramethylene

5 diisocyanate, hexamethylene diisocyanate, 2,2,4-trimethylene diisocyanate, 1,12-dodecane diisocyanate, cyclohexane 1,3- and 1,4-diisocyanates, 1-isocyanato-3,3,5-trimethyl-5-isocyanato-  
10 methylcyclohexane (= isophorone diisocyanate; IPDI), perhydro-2,4'- and/or 4,4'-diphenylmethane diisocyanate, phenylene 1,3- and 1,4-diisocyanates, toluene 2,4- and 2,6-diisocyanates, diphenylmethane 2,4'- and/or 4,4'-diisocyanate, 3,2'- and/or 3,4-diisocyanato-4-methyl-diphenylmethane, naphthalene 1,5- diisocyanate, triphenylmethane 4,4'-triisocyanate, tetramethylxylylene diisocyanate or mixtures of these compounds.

15 In addition to these simple isocyanates, other isocyanates which contain heteroatoms in the radical linking the isocyanate groups are also suitable. Examples of these include polyisocyanates containing carbodiimide groups, allophanate groups, isocyanurate groups, urethane groups, acylated urea groups and biuret groups.

20 The known polyisocyanates which are mainly used in the production of lacquers are particularly suitable for the process according to the invention, e.g. modification products of the above-mentioned simple polyisocyanates which contain 25 biuret, isocyanurate or urethane groups, particularly tris-(6-isocyanatoethyl)-biuret or polyisocyanates containing low molecular weight urethane groups, such as those which can be obtained by the reaction of IPDI present in excess with simple polyhydric alcohols with molecular weights in the range 62-300, particularly with trimethylolpropane. Any mixtures of 30 the above-mentioned polyisocyanates may also of course be used for the production of the products according to the invention.

35 Other suitable polyisocyanates comprise the known prepolymers containing terminal isocyanate groups, such as those which are obtainable by the reaction of the above-mentioned simple polyisocyanates, primarily diisocyanates, with substoichiometric amounts of organic compounds with at least

two groups which are capable of reacting with isocyanate groups. Isocyanates such as these which are preferably used comprise compounds with a total of at least two amino groups and/or hydroxyl groups, and with a number average molecular weight of 300 to 10,000, preferably 400 to 6000. The corresponding polyhydroxyl compounds are preferably used, e.g. the hydroxypolyesters, hydroxpolyethers and/or the acrylic resins containing hydroxyl groups which are known in the art in polyurethane chemistry.

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In these known prepolymers the ratio of isocyanate groups to hydrogen atoms which are reactive towards NCO corresponds to 1.05 to 10:1, preferably 1.1 to 3:1, the hydrogen atoms preferably originating from hydroxyl groups.

15

In addition, the type and quantitative proportions of the starting materials used in the preparation of the NCO prepolymers are preferably selected so that the NCO prepolymers a) have an average NCO functionality of 2 to 4, preferably of 2 to 3, and b) have a number average molecular weight of 500 - 10,000, preferably of 800 - 4000.

Reaction products of monoisocyanates with esters and partial esters formed between polyhydric alcohols and malonic acid are also suitable as A1 compounds, however. Examples of polyhydric alcohols include dihydric to pentahydric alcohols such as ethanediol, the various propane-, butane-, pentane- and hexanediols, polyethylene- and polypropylene diols, glycerine, trimethylolethane and -propane, pentaerythritol, hexanetriol and sorbitol. Examples of suitable monoisocyanates include aliphatic isocyanates such as n-butyl isocyanate, octadecyl isocyanate, cycloaliphatic isocyanates such as cyclohexyl isocyanate, aryl-aliphatic isocyanates such as benzyl isocyanate or aromatic isocyanates such as phenyl isocyanate.

Also suitable are the corresponding malonic esters of OH group-containing acrylic resins, polyesters, polyurethanes, polyethers, polyester amides and imides and/or the reaction products of malonic acid half esters such as malonic acid monoethyl ester with aliphatic and aromatic epoxy resins, e.g. epoxide group-containing acrylate resins, glycidyl ethers of polyols such as hexanediol, neopentyl glycol, diphenylopropene and -methane and hydantoins containing glycidyl groups. Mixtures of these compounds are also suitable.

The following examples of Group A2 illustrate a suitable hardener component, which contains at least two groups corresponding to formula (I)

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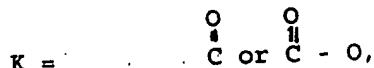
or structural units corresponding to formula (I')

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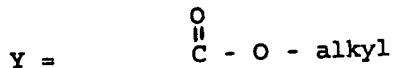
where:

30



and where the latter group is bonded via the C atom to the CR group;

35



and X =

5  $R^1 - \overset{\text{O}}{\underset{\text{||}}{\text{C}}} - \text{CO}_2\text{R}^1, \text{CN}, \text{NO}_2, \text{CONH}_2, \text{CONHR}^1\text{H}, \text{CONR}^1\text{R}^1$ , wherein the  $R^1$  radicals may be the same or different and represent a hydrocarbon radical, preferably an alkyl radical with 1 to 12, most preferably 1 to 6 C atoms, which may also be interrupted by oxygen or an N-alkyl radical,

10  $K' = \overset{\text{O}}{\underset{\text{||}}{\text{C}}} \text{ or } \overset{\text{O}}{\underset{\text{||}}{\text{C}}} - \text{O},$

wherein the latter group is bonded to the CR group via the C atom, and

15  $X' = \overset{\text{O}}{\underset{\text{||}}{\text{C}}} - \text{O} \text{ or } \overset{\text{O}}{\underset{\text{||}}{\text{C}}} - \text{N}.$

20 The number of groups (I) in the hardener according to the invention is preferably 2 to 20, most preferably 2 to 10, the larger numbers relating to oligomeric or polymeric products and representing average values here.

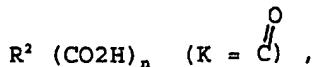
The hardener components A2 which can be used according to the invention preferably correspond to formula (II)

25 
$$\begin{array}{c} X \\ | \\ Y \end{array} \left( \begin{array}{c} \text{CR} - \text{K} - \\ | \\ \text{n} \end{array} \right) \text{R}^2 \quad (\text{II})$$

30 where X, Y and K have the meanings given above,  $R^2$  represents a polyol radical

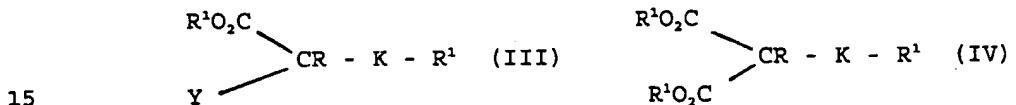
$\text{R}^2 (\text{OH})_n \quad (\text{K} = \overset{\text{O}}{\underset{\text{||}}{\text{C}}} - \text{O})$

35 or the radical  $R^2$  of a polycarboxylic acid



5 and n is at least 2, preferably 2 to 20, most preferably 2 to 10. In the case of oligomeric or polymeric hardener components these numbers are again average values.

10 Also preferred are hardener components which fall within Group A2 and which are obtained by the non-quantitative alcoholysis of compounds of formula (III) or formula (IV)



with polyols  $R^2(Y)_n$ , where Y, K and  $R^1$  have the meanings given above and the  $R^1$  radicals may be the same or different.

20 The above-mentioned polyols R<sub>2</sub>(OH)<sub>n</sub> may be polyhydric alcohols  
which preferably contain 2 to 12, most preferably 2 to 6,  
carbon atoms. Examples of these include: ethylene glycol,  
1,2-, and 1,3-propylene glycol, 1,4- and 2,3-butylene glycol,  
di- $\beta$ -hydroxyethyl butanediol, 1,6-hexanediol, 1,8-octanediol,  
25 neopentyl glycol, 1,6-cyclohexanediol, 1,4-bis-  
(hydroxymethyl)-cyclohexane, 2,2-bis-(4-hydroxycyclohexyl)-  
propane, 2,2-bis-(4-( $\beta$ -hydroxyethoxy)phenyl)propane, 2-methyl-  
1,3-propanediol, glycerine, trimethylolpropane, 1,2,6-  
hexanetriol, 1,2,4-butanetriol, tris-( $\beta$ -hydroxyethyl)-  
30 isocyanurate, trimethylolethane, pentaerythritol and their  
hydroxyalkylation products, and also diethylene glycol,  
triethylene glycol, tetraethylene glycol, polyethylene  
glycols, dipropylene glycol, tripropylene glycol,  
polypropylene glycols, dibutylene glycol, polybutylene glycols  
35 and xylynene glycol. Moreover, polyesters can be used which  
are obtained from or using lactones, e.g.  $\epsilon$ -caprolactones, or  
hydroxycarboxylic acids, such as hydroxypivalic acid,  $\gamma$ -

hydroxydecanoic acid,  $\gamma$ -hydroxycaproic acid or thioglycollic acid, for example. In the case of polyhydric alcohols of this type, the subscript n in the above formula (II) preferably represents 2 to 4.

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Alternatively, the polyol may comprise an oligomeric or polymeric polyol compound (polyol resin), the number average molecular weight  $M_n$  of which (determined by gel chromatography using polystyrene as the calibration standard) is usually in the range from about 170 to 10,000, preferably about 500 to about 5000. However, in special cases  $M_n$  may be 10,000 and above. The oligomers/polymers comprise polymerides, condensation polymers or addition polymer compounds. Their hydroxyl number is generally 30 to 250, preferably 45 to 200, most preferably 50 to 180 mg KOH/g. These compounds, which contain OH groups, may also optionally contain other functional groups such as carboxyl groups.

Examples of polyols of this type include polyether polyols, polyacetal polyols, polyester amide polyols, polyamide polyols, epoxy resin polyols or their reaction products with CO<sub>2</sub>, phenol resin polyols, polyurea polyols, polyurethane polyols, polyols of cellulose esters and ethers, partially saponified homo- or copolymers of vinyl esters, partially acetalated polyvinyl alcohols, polycarbonate polyols, polyester polyols or acrylic resin polyols. Polyether polyols, polyester polyols, acrylic resin polyols and polyurethane polyols are preferred. Polyols of this type, which may also be used in admixture, are described in DE-A-31 30 24 784, for example.

Examples of polyurethane polyols include those which are formed by the reaction of di- and polyisocyanates with an excess of di- and/or polyols. Examples of suitable isocyanates include hexamethylene diisocyanate, isophorone diisocyanate, toluene diisocyanate and also isocyanates formed from three moles of a diisocyanate such as hexamethylene

5 diisocyanate or isophorone diisocyanate, and biurets produced from the reaction of three moles of a diisocyanate with one mole of water, for example. Suitable polyurea polyols may be obtained in a similar manner by the reaction of di- and polyisocyanates with equimolar amounts of amino alcohols, e.g. ethanolamine or diethanolamine.

10 Examples of polyester polyols include the known polycondensation products of di- or polycarboxylic acids or their anhydrides, such as phthalic anhydride, adipic acid, etc., and polyols such as ethylene glycol, trimethylolpropane, glycerine, etc.

15 Suitable polyamide polyols may be obtained in a similar manner to the polyesters, by replacing the polyols at least in part by polyamines such as isophorone diamine, hexamethylene diamine, diethylene triamine, etc.

20 Examples of OH group-containing polyacrylate polyols or polyvinyl compounds include the known copolymers obtained from (meth)acrylic acid esters containing hydroxyl groups or vinyl alcohol and other vinyl compounds, such as styrene or (meth)acrylic acid esters, for example.

25 The above polycarboxylic acids  $R^2(CO_2H)_n$ , where n is preferably 2 to 4 here, may be of an aliphatic, cycloaliphatic, aromatic and/or heterocyclic nature, and may optionally be substituted and/or saturated, by halogen atoms for example. Examples of carboxylic acids such as these and 30 their derivatives include: succinic acid, adipic acid, suberic acid, azelaic acid, sebamic acid, phthalic acid, terephthalic acid, isophthalic acid, trimellitic acid, pyromellitic acid, tetrahydrophthalic acid, hexahydrophthalic acid, cyclohexane 1,3- and 1,4-dicarboxylic acids, tetrachlorophthalic acids, 35 endomethylene tetrahydrophthalic acid and its hexachloro derivative, glutaric acid, maleic acid, fumaric acid, dimeric and trimeric fatty acids such as oleic acid, optionally in

admixture with monomeric fatty acids or cyclic monocarboxylic acids such as benzoic acid, p-tert.-butyl benzoic acid or hexahydrobenzoic acid, and also the reaction products of the above-mentioned polyols  $R^2(OH)_n$  with cyclic carboxylic acid anhydrides.

Depending on the type of the polyol or polycarboxylic acid component, the hardener component A2 which can be used according to the invention comprises more or less viscous liquids, or solids which are substantially soluble at least in the usual lacquer solvents and which preferably contain less than 5 weight %, most preferably less than 1 weight %, of crosslinked constituents. The alcoholysis equivalent weight, which is a measure of the amount of groups (I) or structural units (I') in (A2), is generally between 100 and 5000, preferably between 200 and 2000, and the number average molecular weight  $M_n$  is generally 200 to 10,000, preferably between 500 and 5000 (determined by gel chromatography using polystyrene as the calibration standard). Methods of preparing compounds such as these are described in detail in EP-A-0 310 011.

Additional examples of hardener components which can be used according to the invention are those of Type A3, in which the grouping capable of alcoholysis is derived from a compound containing a  $-CO-CRR^3-COOR^4$  grouping, wherein  $R^3$  is a  $C_1 - C_6$  alkyl or H, preferably hydrogen, and  $R^4$  = alkyl, such as methyl, ethyl, butyl or t-butyl, for example.

The above A3 groupings may be bonded to at least one polyvalent monomeric or polymeric compound. For example, they may be bonded to at least one compound of the group comprising monohydric or polyhydric alcohols, OH-containing polymers, polyamines and polymercaptans. They are polyvalent with respect to their alcoholysis function. They may be prepared, for example, by the esterification of a polyepoxide with a dicarboxylic acid monoester forming the grouping, e.g. malonic

acid monoester. An A3 component with one group capable of alcoholysis for each epoxide group is obtained in this manner. Aromatic or aliphatic polyepoxides may be used for this purpose.

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Further examples of suitable dicarboxylic acid monoethers comprise malonic acid monoalkyl esters and acetone dicarboxylic acid monoalkyl esters, wherein the alkyl radical may be either straight-chain or branched with 1 to 6 C atoms, e.g. methyl, ethyl, n-butyl or t-butyl.

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The hardener components A) may be prepared in the usual solvents. It is advantageous if solvents are used which do not impair the subsequent production of the coating medium.

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It is also advantageous if the content of organic solvents is kept as low as possible. If the hardener component A) contains polar groups, e.g. amide or urethane groupings, it is possible to disperse it easily in water. Moreover, this may optionally be assisted if the crosslinking components contain ionic groups which can be neutralised, e.g. carboxyl groups, in the oligomer or polymer skeleton. Crosslinking agents with ionic groups such as these may be dispersed in water well. At the same time, the content of organic solvents can be reduced to a low value without significantly increasing the viscosity of the crosslinking agent solution.

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One or more (meth)acrylic copolymers or polyester- and/or polyurethane resins are used as component B) in the vehicle composition according to the invention. They contain at least one, preferably at least two,  $\alpha, \beta$ -unsaturated groups bonded via the carbonyl carbon atom of carbonyl, ester and/or amide groups as defined above. In addition, they contain OH groups corresponding to an OH number of up to 350 mg KOH/g, particularly at least one, preferably two, OH groups which can react with the groups of component A) which are capable of alcoholysis. The  $\alpha, \beta$ -unsaturated groups of component B) may be incorporated in the chains of the copolymers or resins.

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They may also preferably be side groups and/or terminal groups. Suitable B) compounds are described in DE-PS-835 809, in US-PS-4 408 018 and in EP-OS- 16 16 79 and EP-OS- 22 41 58, for example, to which reference is made here. These are B) compounds with at least two groups corresponding to the formula



10 in which:

15  $R^5$  represents hydrogen or a hydrocarbon radical, preferably an alkyl radical with 1 to 12, most preferably 1 to 4, C atoms such as a methyl, ethyl, n-propyl, iso-propyl, n-butyl or tert.-butyl group;

20  $R^4$  denotes entities which are the same or different, representing hydrogen, a hydrocarbon radical, preferably an alkyl radical with 1 to 10, most preferably 1 to 4, C atoms, an ester group  $-CO_2R^1$ , a  $-CN$ ,  $-NO_2$ ,  $-SO_2-$ ,  $-CONHR^1$ ,  $-CONR^1R^2$  or  $-COR^1$  group, wherein the  $R^1$ 's are the same or different and are as defined above for formula I; and

25  $Z$  represents  $\begin{array}{c} O \\ || \\ -C - \end{array}$ ,  $\begin{array}{c} O \\ || \\ -C - O - \end{array}$ , or  $\begin{array}{c} O \\ || \\ -C - N - \end{array}$ ,

wherein the two latter groups are bonded to the  $CR^4$  group via the C atom.

30  $R^5$  and  $R^4$  in the above  $R^5 R^4 - C$  group preferably each represent hydrogen.

35 The  $R^5 R^4 C = CR^4 - Z$  group (V) may be derived from a mono- or multiply-unsaturated mono- or dicarboxylic acid with 2 to 20, preferably 3 to 10, C atoms, for example.

Examples of carboxylic acids such as these include crotonic acid and citraconic acid or their anhydrides, sorbic acid, fumaric acid, mesaconic acid, substituted and unsubstituted cinnamic acids, dihydrolevulinic acid, malonic acid mononitrile,  $\alpha$ -cyanacrylic acid, alkylidene malonic acid, alkylidene acetoacetic acid, and preferably acrylic acid, methacrylic acid and/or maleic acid or their anhydrides. The linkage to a polymeric carrier which is possible via the group Z or also via the R<sup>4</sup> radical may be effected via ester, amide, urethane or urea groups.

In accordance with the above, the groups corresponding to formula (V) may be bonded to the radical of a polyol, a polyamine, a polyamide or a polyiminoamide, wherein this radical may also be oligomeric or polymeric.

The polyols concerned here are basically the same as those listed in detail above in connection with component A), i.e. polyhydric alcohols or oligomeric or polymeric polyol compounds, e.g. polyether polyols, polyester polyols, acrylic resin polyols and polyurethane polyols.

Moreover, the  $\alpha, \beta$ -unsaturated group which is bonded via a carbonyl carbon atom may be bonded to polymers, e.g. condensation polymers such as polyesters or addition polymers such as polyurethanes, polyethers or (meth)acrylic copolymers or vinyl polymers, such as glycidyl (meth)acrylate copolymers. Polymers which should be mentioned here by way of example include urethane acrylates, obtained by the reaction of polyisocyanates such as hexamethylene diisocyanate with hydroxyalkyl acrylates such as hydroxyethyl acrylate, or by the reaction of hydroxyl group-containing polyesters, polyethers or polyacrylates with polyisocyanates and hydroxyalkyl acrylates, urethane acrylates obtained by the reaction of caprolactonediol or -triol with polyisocyanates and hydroxyalkylacrylates, polyether acrylates obtained by the esterification of hydroxypolyethers with acrylic acid,

5 polyester acrylates obtained by the esterification of hydroxypolyesters with acrylic acid, polyacrylates obtained by the reaction of acrylic acid with vinyl polymers containing epoxide groups, e.g. copolymers of glycidyl (meth)acrylate or vinyl glycidyl ether. The term "(meth)acrylic" is to be understood, both here and below, as representing acrylic and/or methacrylic.

10 Mixtures of the above compounds may also be used as component B).

15 The C=C equivalent weight of component B) is 85 to 1800, for example, preferably 180 to 1200, and the number average molecular weight ( $M_n$ ) is 170 to 10,000, for example, preferably 500 to 5000. Component B) has an OH number less than 350, most preferably from 20 to 200 mg KOH/g.

20 Like component A), component B) is preferably substantially free from primary, secondary and tertiary amino groups.

25 The coating media used according to the invention contain 0.1 - 10 weight % of thermally and/or photochemically activatable initiators, which form free radicals on decomposition, as component C). The amount used is preferably 0.1 to 6 weight %, based on the total amount of components A) and B).

30 The usual thermally activatable initiators which are familiar to one skilled in the art may be used as thermally activatable initiators, such as the usual peroxides, such as di-tert.-butyl peroxide, tertiary butyl perbenzoate or tertiary butyl peroctoate, for example; hydroperoxides, such as tertiary butyl hydroperoxide or cumene hydroperoxide, for example; and azo compounds, such as azo-bis-isobutyronitrile, for example. However, initiators with labile carbon-carbon bonds are preferred (so-called C-C initiators), such as benzpinacol derivatives, e.g. benzpinacol, benzpinacol disilyl ether

(monomeric or oligomeric), benzpinacol dimethyl ether, and also tetraphenylethane and tetraphenylethane dinitrile.

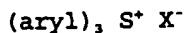
5 The vehicle compositions according to the invention may also contain the usual photo-initiators, such as those which are known for radical and ionic polymerisation, as component C). Suitable examples comprise initiators which absorb in the wavelength region from 190 to 400 nm.

10 Examples of radical initiators which can be used include chlorine-containing initiators such as chlorine-containing aromatic compounds, e.g. those described in US-A-4 089 815; aromatic ketones as described in US-A-4 318 791 and EP-A-0 161 463; hydroxyalkyl phenones as described in US-A-4 347 111; 15 water-soluble initiators, for example those based on hydroxyalkyl phenones as described in US-A-4 602 097; unsaturated initiators such as OH-functional aromatic compounds, which may be esterified with acrylic acid, for example, as described in US-A-3 929 490, EP-A-0 143 201 and 20 EP-A-0 341 560; or combinations of these types of initiators, as described in US-A-4 017 652, for example.

25 Particular examples include 2-methyl-2-hydroxy-propiophenone, benzophenone, thioxanthone derivatives, acylphosphine oxides and Michler's ketone.

30 Radical initiators which are most preferably used comprise phosphine oxides and combinations of phosphine oxides with other customary initiators, as described above.

35 Examples of cationic initiators which can be used comprise triarylsulphonium salts corresponding to the general formula:



35 wherein aryl represents an aryl radical such as the phenyl radical, and X<sup>-</sup> is an anion such as SbF<sub>6</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup> or BF<sub>4</sub><sup>-</sup>.

as described in US-A-4 417 061, EP-A-0 327 194 and DE-A-2 904 626. Other examples of cationic initiators include oxonium salts, iodonium salts and diazonium salts, such as those described in the following literature references; EP-A-0 161 5 131, US-A-4 421 904, EP-A-0 145 633, EP-A-0 310 881, EP-A-0 310 882 (iodonium salts); DE-A-3 808 590 and DE-A-3 808 951 (diazonium salts).

10 In addition to these initiators, metallocene complexes, such as those described in EP-A-0 094 915, for example, may also be used.

15 The coating media according to the invention contain 0 to 20 weight % of one or more commercially available melamine resins as component D1). These melamine resins may be etherified with methanol, butanol or iso-butanol or mixtures thereof, such as the commercial products Setamine VS 138, Maprenal MF 610, Cymel 254, Cymel 301 and Cymel 303, for example.

20 The coating media according to the invention may contain one or more blocked polyisocyanates as crosslinking agents (component D2). Examples of polyisocyanates which can be used to form the basis of the blocked polyisocyanates include cycloaliphatic, aliphatic or aromatic polyisocyanates such as 25 tetramethylene diisocyanate, hexamethylene diisocyanate, 2,2,4-trimethylene diisocyanate, 1,12-dodecane diisocyanate, cyclohexane 1,3- and 1,4-diisocyanates, 1-isocyanato-3,3,5-trimethyl-5-isocyanato-methylcyclohexane (= isophorone diisocyanate; IPDI), perhydro-2,4'- and/or 4,4'-diphenylmethane diisocyanate, phenylene 1,3- and 1,4-diisocyanates, toluene 2,4- and 2,6-diisocyanates, diphenylmethane 2,4'- and/or 4,4'-diisocyanate, 3,2'- and/or 30 3,4-diisocyanato-4-methyl-diphenylmethane, naphthalene 1,5-diisocyanate, triphenylmethane 4,4'-triisocyanate, 35 tetramethylxylylene diisocyanate or mixtures of these compounds.

In addition to these simple isocyanates, other isocyanates which contain heteroatoms in the radical linking the isocyanate groups are also suitable. Examples of these include polyisocyanates containing carbodiimide groups, 5 allophanate groups, isocyanurate groups, urethane groups, acylated urea groups and biuret groups.

The known polyisocyanates which are mainly used in the 10 production of lacquers are particularly suitable for the process according to the invention, e.g. modification products of the above-mentioned simple polyisocyanates which contain 15 biuret, isocyanurate or urethane groups, particularly tris-(6-isocyanatoethyl)-biuret or low molecular weight polyisocyanates containing urethane groups, such as those which can be obtained by the reaction of IPDI present in excess with simple polyhydric alcohols with molecular weights in the range 62-300, particularly with trimethylolpropane. Any mixtures of the above-mentioned polyisocyanates may also 20 of course be used for the production of the products according to the invention.

Other suitable polyisocyanates comprise the known prepolymers 25 containing terminal isocyanate groups, such as those which are obtainable by the reaction of the above-mentioned simple polyisocyanates, primarily diisocyanates, with substoichiometric amounts of organic compounds with at least 30 two groups which are capable of reacting with isocyanate groups. Isocyanates such as these which are preferably used comprise compounds with a total of at least two amino groups and/or hydroxyl groups, and with a number average molecular 35 weight of 300 to 10,000, preferably 400 to 6000.

In these known prepolymers the ratio of isocyanate groups to 35 hydrogen atoms which are reactive towards NCO corresponds to 1.05 to 10:1, preferably 1.1 to 3:1, the hydrogen atoms preferably originating from hydroxyl groups.

In addition, the type and quantitative proportions of the starting materials used in the preparation of the NCO prepolymers are preferably selected so that the NCO prepolymers a) have an average NCO functionality of 2 to 4, 5 preferably of 2 to 3, and b) have a number average molecular weight of 500 - 10,000, preferably of 800 - 4000.

The isocyanate groups of the polyisocyanates are completely blocked. The usual blocking agents, such as those which are 10 used in the lacquer industry for example, may be used as blocking agents. Examples of blocking agents which may be used include malonic acid dimethyl ester, malonic acid diethyl ester, acetoacetic acid ethyl ester, epsilon-caprolactam, acetanilide, acetylacetone, acetonoxime, 1,2-propanediol 15 and/or butanone oxime, the last-mentioned blocking agent being preferred.

Blocking of the polyisocyanates may be effected, for example, 20 by heating one or more polyisocyanates with the blocking agent. For example, one or more polyisocyanates may be selected and heated with stirring, e.g. to about 80°C, whereupon the blocking agent is added (over about 10 minutes, for example). Stirring is continued until the NCO number is less than 0.1 %. It is also possible to block one or more 25 polyisocyanates with a mixture of two or more blocking agents.

The advantage of using two or more different polyisocyanates and/or two or more different blocking agents is that this 30 enables crosslinking to take place over a wide temperature range.

The coating media according to the invention may contain  $\alpha, \beta$ -unsaturated reactive thinners as component E) for adjusting the viscosity. These are free from hydroxyl groups. They are 35 generally liquid at room temperature and are preferably of low viscosity.

Examples of reactive thinners such as these include (meth)acrylates, such as lauryl (meth)acrylate for example; alkyl glycol di(meth)acrylates such as ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, 5 propylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate; 1,6-hexamethylene di(meth)acrylate, trimethylolpropane tri(meth)acrylate, triethylolpropane triethoxy tri(meth)acrylate, pentaerythritol tetra(meth)acrylate and ethoxylated and propoxylated variants, 10 or 2-acetoacetoxyethyl (meth)acrylate.

The term "(meth)acrylate" is understood to mean acrylate and/or methacrylate or acrylato- and/or methacrylato- in the present description and in the claims.

15 The coating media according to the invention may contain hydroxyfunctional compounds as component F). These are selected, for example, from

- 20 a) polyols with at least two hydroxyl groups (i.e. including diols, triols, etc.) from the group comprising straight chain or branched alkanediols and polyols with 2 to 12 carbon atoms, or
- 25 b) hydroxyl group-containing poly(meth)acrylates or poly(meth)acrylamides based on (meth)acrylic acid hydroxyalkyl esters with 2 to 12 carbon atoms in the alkyl portion or (meth)acrylic acid hydroxyalkyl amides with 2 to 12 carbon atoms in the alkyl portion, 30 optionally copolymerised with  $\alpha, \beta$ -unsaturated monomers, with a number average molecular weight  $M_n$  of 1000 to 10,000 g/mole, or
- 35 c) polyester polyols or polyether polyols, each with a number average molecular weight  $M_n$  of 500 to 2000 g/mole.

Examples of alkane di- and polyols of Group a) are those with straight and branched chains with 2 to 12 carbon atoms. They contain at least two hydroxyl functions, preferably at least three, however. Examples of these include propanediol, 5 butanediol, hexanediol, glycerine, trimethylpropane and pentaerythritol.

Examples of hydroxyl group-containing poly(meth)acrylates b) comprise those based on (meth)acrylic acid hydroxyalkyl esters of acrylic acid or methacrylic acid with alcohols with at least two hydroxyl groups, such as 1,4-butanediol mono(meth)acrylate, 1,6-hexanediol mono(meth)acrylate or 1,2,3-propanetriol mono(meth)acrylate. Examples of hydroxyl group-containing poly(meth)acrylamides b) based on (meth)acrylic acid hydroxyalkylamides include amides of acrylic acid or methacrylic acid with hydroxyalkylamines or di(hydroxyalkyl)amines, each with 2 to 12 carbon atoms in the alkyl portion, and which may contain one or more hydroxyl groups, such as acrylic acid hydroxyethylamide.

20 The hydroxyl group-containing poly(meth)acrylates of component b) may be homopolymers or copolymers. They preferably have a number average molecular weight of 1000 to 10,000, most preferably from 3000 to 6000 g/mole. Copolymerisable monomers, 25 for preparing the copolymers include  $\alpha, \beta$ -unsaturated monomers, radically polymerisable monomers from the group comprising esters of  $\alpha, \beta$ -unsaturated carboxylic acids such as acrylic acid or methacrylic acid, examples of the alcohol component comprising methyl, ethyl and propyl alcohols and their isomers and higher homologues. Other examples comprise diesters of 30 maleic or fumaric acid, the alcohol component being the same as that mentioned above. Further examples include vinyl aromatic compounds such as styrene,  $\alpha$ -methyl styrene and vinyl toluene. Other examples include vinyl esters of short chain 35 carboxylic acids, such as vinyl acetate, vinyl propionate and vinyl butyrate. It is also possible to use silane-modified monomers, such as gamma-methacryloxypropyl trimethoxy-silane

or gamma-methacryloxypropyl-tris-(2-methoxyethoxy-silane, for example.

5 The coating medium according to the invention comprises a mixture of components A, B, D, E and F and the radical initiator C). The vehicles are compatible with each other and may be mixed with solvents for better miscibility. Solvents which do not subsequently have a negative effect in the lacquer are preferred for this purpose.

10 Components A) to F) or mixtures thereof may be used in solvent-containing form according to the invention. However, it is also possible to produce aqueous coating media. The components may be converted into an aqueous phase for this 15 purpose, optionally with low proportions of solvents and optionally together with emulsifying agents. It is also possible, of course, to use water-soluble components A to F.

20 The preferred solvents are those which are miscible with water. The amount of solvent may be up to 20 weight % for example, preferably up to 10 weight %, based on the final aqueous composition. Ionic or non-ionic emulsifying agents, preferably non-ionic emulsifying agents, may be used as the emulsifying agents. The content of emulsifying agent may be 25 0.5 to 30 weight % for example, preferably between 1.5 and 15 weight %, based on the solids content of components A to F in the aqueous coating medium.

30 The usual methods familiar to one skilled in the art may be employed for the preparation of the aqueous dispersions. Thus, for example, the solvent-containing forms of the components or mixtures thereof may be substantially freed from solvents, preferably by distillation under reduced pressure, whereupon the emulsifying agent can be dispersed therein, 35 preferably in the resins or resin mixtures whilst the latter are still warm and of low viscosity. This mixture can then be added to the aqueous phase, with intensive mixing for

example. The preparation of the dispersion may also be assisted by heating the aqueous phase. Examples of suitable mixer units include high speed stirrers or rotor/stator mixers. It is also possible to improve the quality of the dispersion by means of high-pressure or ultrasonic homogenisers.

5 The process may be carried out continuously or batch-wise. The dispersions produced may also be mixed with each other at 10 this time. An aqueous oil-in-water dispersion is obtained which is stable on storage and which can be adjusted with water to give lower solids contents which are suitable for application. The aqueous dispersions obtained according to 15 the invention may have a solids content in the range of 25 - 70 weight %, for example, based on the final dispersion. They may optionally be diluted with water for application, e.g. to a viscosity suitable for spraying.

20 Commercially available ionic or non-ionic emulsifying agents are suitable as emulsifying agents. For example, the reaction products of alkyl phenols with alkylene oxides may be used, as may the reaction products of sorbitane fatty acid esters with alkylene oxides, e.g. C<sub>1</sub> - C<sub>12</sub> alkylphenol ethoxylates.

25 Solvent-based coating media preferably have a vehicle content of up to 70 weight %, most preferably up to 60 weight %. The lower limit is preferably greater than 30 weight %, based on the final coating medium in each case.

30 The coating media according to the invention may be produced from the individual components by the usual methods familiar to one skilled in the art. For the production of the coating media, the usual industrial lacquer additives may optionally be added to the crosslinking and vehicle components which are 35 used according to the invention. Examples of such additives include anti-crater agents, anti-foaming agents, flow media, anti-settling agents, viscosity regulators, UV stabilisers and

bonding agents. The properties affecting application and film formation can be influenced by the amount of additives.

Known pigments and/or extenders may optionally also be incorporated in the coating media. The relevant methods, e.g. dispersion or milling, have frequently been described in the literature. The usual pigments for primers, extenders, clear or covering lacquers are suitable as pigments, for example carbon black, titanium dioxide, finely dispersed silica, aluminium silicate, French chalk, organic and inorganic coloured pigments, transparent colorants, metallic pigments or crosslinked polymer microparticles. Metallic lacquers, coloured covering lacquers or clear lacquers may be produced depending on the pigments and extenders selected.

The coating media according to the invention may contain organic solvents. These serve to adjust the viscosity on application and to influence the flow behaviour, and also to achieve a given lacquer effect. Examples of such solvents include aromatic hydrocarbons, e.g. xylene; aliphatic hydrocarbons, e.g. n-hexane or cyclohexane; ketones, such as acetone or methyl isopropyl ketone, for example; esters, such as butyl acetate or ethyl acetate, for example; ethers, such as methoxypropanol or butoxypropanol; or alcohols, such as isopropanol, hexanol or ethyl glycol, for example. The properties relating to application and flow behaviour can be influenced by the boiling point or the different dissolving powers of the solvents. The amount of solvent added thus depends on the desired properties, particularly on the viscosity properties, of the coating medium. True solutions, emulsions or dispersions are formed when water is used as the solvent. Coating media which contain water have a particularly low content of volatile organic constituents.

The coating media according to the invention are single-component systems. They are characterised by high storage stability and can be stored for more than six months without

significant changes in viscosity. Metallic substrates, plastics, wood or substrates previously provided with coatings are suitable as substrates.

5 The coating media according to the invention may be aqueous or non-aqueous. In the aqueous system it is possible optionally to incorporate the additives in the aqueous dispersion of component A) or of component B). These components may optionally be mixed before application to form 10 coating media. However, it is preferably also possible to produce aqueous single-component systems.

15 The coating media produced in this manner may be applied in the usual way, for example by spraying, immersion, by roller or via a doctor blade. The covering lacquer coating is applied to the substrate, which is optionally already provided with further lacquer layers. After a venting-off phase (at up to 80°C) the applied coating medium is crosslinked by heating. The stoving temperature is between 80 and 180°C, 20 preferably between 110 and 150°C. When the material contains photochemically activatable initiators, hardening by irradiation, using UV light for example, may be effected at the same time as or following stoving. The layer thickness of the stoved film is about 15 - 50 µm. A hard, cross-linked, 25 glossy, acid-resisting lacquer coating is produced in this manner. One preferred embodiment is the application of the coating medium according to the invention as a clear lacquer coating on a base lacquer, preferably an aqueous base lacquer. This operation may be carried out wet-in-wet, or the base 30 lacquer may be previously dried by heating. This results in particularly good bonding of the two layers.\*

35 Base lacquers which contain the usual covering lacquer pigments may be over-coated with coating media formulated as clear lacquers according to the invention, for example. The base lacquers preferably contain special effect pigments, such

\* Insert page 28a.

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28a

It is possible to heat the lacquer, e.g. to 60 to 100°C and to apply it while hot. This reduces the viscosity of the lacquer and it can be applied with a high solids content.

It is also possible to add super-critical carbon dioxide as a solvent to the lacquer and to apply it in accordance with the so-called Unicarb process, which, e.g. is described in EP-A 0 321 607 and in EP-A 0 388 927.

as metallic pigments, for example. Polyester or polyurethane- or acrylic resins are preferably used as the basis of the vehicle for the base lacquer. Binders such as these may optionally be crosslinked via crosslinking agents, e.g. 5 melamine or isocyanate derivatives.

The coating media according to the invention are particularly suitable for clear lacquers or covering lacquers; these are 10 preferably used in the motor vehicle industry, but may also be used in other fields. The use of the coating medium according to the invention in multilayer coatings is particularly suitable for the coating of mass-produced 15 automobiles. However, it may be used for other purposes, such as for domestic appliances for example, or in the furniture industry, in order to obtain coatings which are particularly stable towards acids.

The following examples serve to explain the invention. All 20 parts (pts.) and percentages (%) are given by weight.

Example 1

**Preparation of a resin with groups capable of alcoholysis (component A)**

25 807 pts. of a commercially available polycaprolactonetriol (CAPA305, Registered Trade Mark of Interox Chem. Ltd.) were reacted at 80°C in a reaction vessel with 700 pts. butyl acetate, 350 pts. Solvesso 100 (a mixture of aromatic hydrocarbons - Registered Trade Mark) and 995 pts. 3- 30 isocyanato-methyl-3,5,5-trimethyl-cyclohexyl isocyanate until an NCO content of 6.6 weight % was obtained. 637 pts. acetoacetic acid ethyl ester were then added and the mixture was maintained at 100°C in the presence of 10 pts. zinc acetylacetone until an NCO content of less than 0.1 weight % was obtained.

35 The resin had a viscosity of 1500 mPas (25°C).

Example 2**Preparation of an acryloyl-functional resin (component B)**

5 a) 1000 pts. xylene were placed in a 4 litre three-necked flask fitted with a stirrer, thermometer, dropping funnel and reflux condenser and heated to 90°C with stirring. A mixture of

10 380 pts. glycidyl methacrylate  
128 pts. butyl methacrylate  
252 pts. butyl acrylate  
200 pts. styrene and  
40 pts. tert.-butyl peroctoate

15 was added drop-wise over 5 hours. The epoxy-functional resin obtained had a viscosity of 70 mPas (25°C) and a solids content of 50.1 % (1h/150°C).

20 b) 800 pts. of this resin were heated with stirring to 90°C in a two litre flask fitted with a stirrer, thermometer, dropping funnel and reflux condenser. A mixture of 50 pts. acrylic acid and 1 pt. triphenyl phosphite was added drop-wise at this temperature over 20 minutes, and thereafter the reaction was allowed to proceed until an acid number of 1 mg KOH/g was obtained. The mixture was then concentrated under vacuum to give a solids content of 60 weight %.

30 Examples 3a to 3f

**Preparation of clear lacquer compositions**

35 The following clear lacquer compositions 3a to 3f were prepared using components A and B as prepared in the two Examples 1 and 2, respectively, and using a commercially

available oligomeric benzpinacol silyl ether as a radical initiator (component C):

	Clear lacquer	1 (component A)	2b (component B)	3 (component C)
5				
	3a	10 pts.	90 pts.	0 pts.
	3b	10 pts.	90 pts.	3 pts.
	3c	20 pts.	80 pts.	0 pts.
	3d	20 pts.	80 pts.	3 pts.
10	3e	40 pts.	60 pts.	0 pts.
	3f	40 pts.	60 pts.	3 pts.

The clear lacquers were applied using a doctor blade to glass plates to give a dry film thickness of 30  $\mu\text{m}$  and stoved for 15 20 minutes at 140°C. The degree of crosslinking was determined by measuring the pendulum hardness (König) before and immediately after a ten-minute exposure to xylene and after a 2-hour regeneration period. The comparative samples without a radical initiator exhibited significantly greater softening under the effect of xylene than the samples with a radical initiator according to the invention.

**Pendulum hardness (König) in seconds**

	Clear lacquer	before xylene	immediately after	after a 2-hour
25		treatment	xylene treatment	regeneration
	3a	72	52	11
	3b	183	79	121
	3c	145	47	14
30	3d	196	156	166
	3e	204	31	18
	3f	218	190	199

**Example 4**

35

**Preparation of an aqueous clear lacquer**

a) Components A, B and C were mixed as defined in Example 3 in the amounts according to Example 3f and

concentrated under vacuum at a maximum temperature of 60°C to give a solids content of 80 weight %.

5 b) 155.2 pts. of a 10 % aqueous solution of an emulsifying agent based on a polyoxypropylene polyoxyethylene sorbitanic acid diester were placed in a 1 litre flask at 60°C. The mixture was stirred using a stirrer rotating at about 8500 rpm. 388 pts. of the vehicle mixture prepared as in 4a were added at 60°C over 3  
10 minutes. 50 pts. demineralised water were added. The milky-white emulsion obtained had a solids content of 54.5 weight %.

15 c) Clear lacquer composition:

77.9 pts. of the emulsion from 4b  
22.1 pts. demineralised water.

20 The aqueous clear lacquer had a solids content of 42.4 weight %. It was applied using a spray-gun (1.3 mm nozzle) to give a dry film thickness of about 50  $\mu\text{m}$  to blank sheet steel or to a steel sheet provided with a multilayer coating comprising electro-dip primer, extender and aqueous base lacquer, and was  
25 stoved for 20 minutes at 140°C after a 20-minute vent-off phase (10 minutes at room temperature, 10 minutes at 80°C).

The stoved film had a high hardness, good resistance to solvents and a good appearance.

30 Properties:

on sheet steel Pendulum hardness: 170 s  
MEK rub: >100

35 In built-up structure: Gloss (20°C): 87  
Pendulum hardness: 117 s  
 $\text{H}_2\text{SO}_4$  (100%, 65°C): first slight effect visible

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33

after 13  
minutes

Cross-cutting  
5 test: Characteristic very good to good

Herberts Gesellschaft mit beschränkter Haftung

5

**CLAIMS**

1. A vehicle composition, containing

10 A) 10 - 90 weight % of one or more compounds acting as crosslinking agents with an average of at least two groups capable of alcoholysis,

15 B) 10 - 90 weight % of one or more (meth)acrylic copolymers, polyester- and/or polyurethane resins with at least one  $\alpha, \beta$ -unsaturated group bonded via the carbonyl carbon atom of

20 
$$\begin{array}{c} \text{O} \quad \text{O} \quad \text{O} \\ || \quad || \quad || \\ -\text{C}-, -\text{C}-\text{O}- \text{ and/or } -\text{C}-\text{N}- \end{array}$$
,

25 with a C=C equivalent weight of 85 - 1800, a number average molecular weight ( $M_n$ ) of 170 - 10,000 g/mole, and an OH number of up to 350 mg KOH/g, wherein the weight percentages of components A and B are each based on the solid and add up to 100 weight %, and

30 C) 0.1 - 10 weight % of one or more thermally and/or photochemically activatable initiators,

35 D1) 0 - 20 weight % of one or more melamine resin crosslinking agents,

D2) 0 - 40 weight % of one or more blocked polyisocyanates,

E) 0 - 40 weight % of one or more (meth)acryloyl-functionalised reactive thinners which are free from OH groups,

5 F) 0 - 30 weight % of one or more diols, triols, polyols and/or hydroxyfunctional polyethers, polyesters and/or (meth)acrylic copolymers

10 and optionally solvents, the usual lacquer additives, optionally water, optionally pigments and optionally extenders,

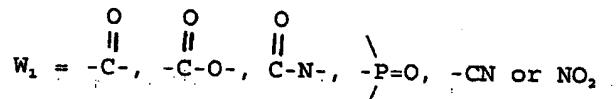
15 wherein the weight percentages of components C), D1), D2), E) and F) are each based on the solid and on the sum of the weight percentages of components A) and B).

2. A vehicle composition according to claim 1, wherein the crosslinking component A) contains on average at least 20 two of the following groups, which may be the same or different:

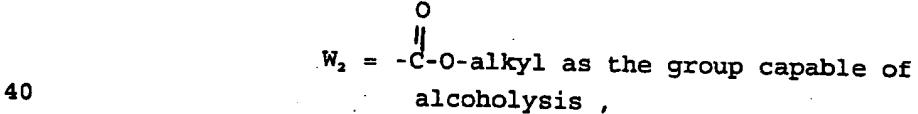


25 where  $R = H$ , alkyl or aryl,

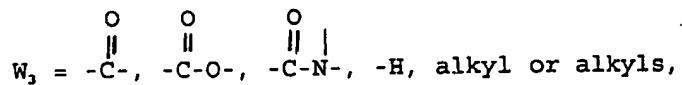
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10       wherein the  $-\text{C}-\text{O}-$  and  $-\text{C}-\text{N}-$  radicals are each bonded via the carbon atom on the CR group and the CR group is bonded via at least one of the radicals  $W_1$  and/or  $W_3$  to a polymeric or oligomeric unit.

15       3. A vehicle composition according to either one of claims 1 or 2, characterised in that it exists in solvent-free form.

20       4. A vehicle composition according to either one of claims 1 or 2, characterised in that it exists in solvent-containing form.

25       5. A vehicle composition according to any one of claims 1, 2, 3 or 4, characterised in that it exists in aqueous form.

30       6. A coating medium containing the vehicle composition according to any one of claims 1 to 5 and in addition one or more organic solvents and/or water, and pigments and/or extenders and optionally the usual lacquer additives.

35       7. A coating medium according to claim 6 in aqueous form with a solvent content of 0 to 20 weight % based on the total coating medium.

8. A coating medium according to claim 6 or 7 containing water and one or more emulsifying agents.

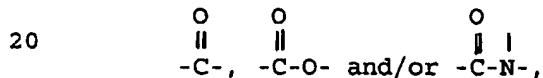
9. A process for producing coatings by the application of a coating medium to a substrate to be coated and the subsequent thermal hardening of the coating obtained, characterised in that a coating medium according to one of claims 6 to 8 is applied and hardening is carried out at temperatures of 80 to 180°C.
10. A process for producing multilayer coatings by the application of a base lacquer to a substrate to be coated, optionally a brief aeration and the wet-in-wet application of a clear lacquer and subsequent joint hardening, characterised in that a coating medium according to one of claims 6 to 8 is used as the base lacquer and/or clear lacquer.
15. A process according to claim 9 or 10, characterised in that an initiator with labile C-C bonds is used as component C).
20. The use of the vehicles according to any one of claims 1 to 5 or of the coating media according to any one of claims 6 to 8 in the production of acid-resisting clear or covering lacquer coatings, base lacquer coatings, extender layers and/or primers.
25. A use according to claim 12 for the production of clear or covering lacquer coatings, extender layers and/or primers in multilayer coatings.
30. The use of the vehicles according to any one of claims 1 to 5 or of the coating media according to any one of claims 6 to 8 in the coating of motor vehicles.

Herberts Gesellschaft mit beschränkter Haftung

5 **Abstract**

A vehicle composition which results in acid-resisting coatings is described. The vehicle composition contains:

10 A) 10 - 90 weight % of one or more compounds acting as crosslinking agents with an average of at least two groups capable of alcoholysis,  
B) 10 - 90 weight % of one or more (meth)acrylic copolymers, polyester- and/or polyurethane resins with  
15 at least one  $\alpha, \beta$ -unsaturated group bonded via the carbonyl carbon atom of



25 with a C=C equivalent weight of 85 - 1800, a number average molecular weight ( $M_n$ ) of 170 - 10,000 g/mole, and an OH number of up to 350 mg KOH/g, wherein the weight percentages of components A and B are each based on the solid and add up to 100 weight %, and

C) 0.1 - 10 weight % of one or more thermally and/or photochemically activatable initiators,  
30 D1) 0 - 20 weight % of one or more melamine resin crosslinking agents,  
D2) 0 - 40 weight % of one or more blocked polyisocyanates,  
E) 0 - 40 weight % of one or more (meth)acrylol-functionalised reactive thinners which are free from OH groups,  
35 F) 0 - 30 weight % of one or more diols, triols, polyols and/or hydroxyfunctional polyethers, polyesters and/or (meth)acrylic copolymers, and optionally solvents, the

usual lacquer additives, optionally water, optionally  
pigments and optionally extenders,

5 wherein the weight percentages of components C), D1),  
D2), E) and F) are each based on the solid and on the  
sum of the weight percentages of components A) and B).

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